materials for solar cells [13]. A review of research on the current–voltage characteristics of solar cells sensitized by polymethine dyes is presented in the work of Mishra et al. [14].

Recently, a long-range inductive-resonant electronic excitation energy transfer between dye molecules adsorbed on a film of TiO_2 was proposed to improve the light-harvesting characteristics of solar cells [15–20]. In solar cells, the donor (fluorescent material) absorbs high-energy photons and transmits them through the Förster resonance energy transfer (FRET) to acceptor (sensitizing dye), as shown in Fig. 1.

McGehee' group [18] developed a comprehensive model to compute the excitation transfer efficiency in a dye-sensitized solar cell for pores with cylindrical or spherical geometries and showed that the energy transfer process can be over 90% efficient in a dye-sensitized solar cell with dyes with reasonable properties. The application of FRET has the advantages of both enhancing light absorption and improving charge separation and provides a way to improve exciton harvesting by placing the exciton close to the heterojunction interface.

The energy transfer efficiency is determined by several factors, including the overlap integral of the fluorescence spectra of the donor and the acceptor absorption, the quantum yield of the energy donor, and the distance between the interacting molecules. Dye-sensitized solar cell using dyes, such as ruthenium-based and zinphthalocyanine, were explored based on the FRET idea [21,17]. Siegers et al. [20] demonstrated the use of Förster-resonant energy transfer (FRET) between covalently linked energy donor molecules to the SD attached to the titania surface. These traditional sensitizing dyes (SD) made from ruthenium-based complexes have low molar extinction coefficients (5000–20,000 M^{-1} cm^{-1}). However, organic and polymethine dyes [8] have demonstrated substantially higher molar extinction coefficients (100,000–300,000 M^{-1} cm^{-1}) and are good choices for designing dye-sensitized solar cells.

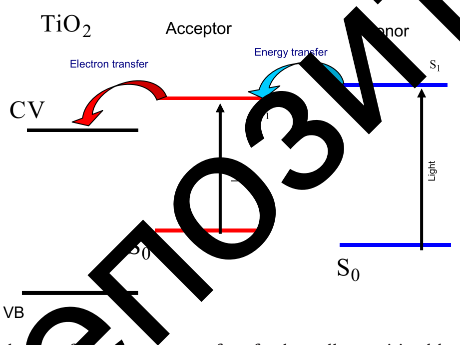

Fig. 1. Scheme of the energy transfer of solar cells sensitized by donor–acceptor compounds.

This paper demonstrates the ability to improve the electrophysical parameters of photovoltaic cells sensitized with organic dyes through the electronic excitation energy transfer between molecules of metal-free dyes directly into the solar cell. FRET between rhodamine and the new polymethine dyes adsorbed into the semiconductor TiO_2 films was studied. It was shown that the photovoltaic parameters of cells sensitized by donor–acceptor compounds improved in comparison with cells sensitized by neat acceptors.

2. Experimental part

The organic dyes, Rhodamine 6G myristate and polymethine dye, were chosen as the donor and acceptor of energy, respectively. Rhodamine dye was synthesized in the Institute of Organic Intermediates and Dyes (NIOPIK, Russia), and squarylium dye (SQ) in the Institute of Organic Chemistry, National Academy of Sciences of Ukraine (Ukraine). Dyes were used without additional purification. The structural formulae of the compounds are shown in Fig. 2. SQ dye was chosen as the energy acceptor and the main sensitizer of the solar cell because of its optimal arrangement of HOMO–LUMO orbitals with respect to the conduction band of TiO_2.

The results of the calculation performed by the INDO method have shown that the HOMO orbital of the dye has an energy of about −6.22 eV and the LUMO orbital energy is equal to −0.80 eV. It is evident that the polymethine dye may act as an electron donor with respect to TiO_2.

The absorption and fluorescence spectra of the dye solutions and TiO_2 films were measured with a CM2203 spectrometer (Solar, Belarus). The excited-state lifetime of the donor and acceptor was measured using a pulsed spectrofluorimeter with picosecond resolution with registration in time-correlated photon counting mode (Becker & Hickl, Germany).

Solar cells were prepared and assembled according to a previously described procedure [22]. Glass substrates coated with a layer of conductive FTO were purchased from Sigma-Aldrich. Pastes "Ti-nanoxide HT" and "Ti-nanoxide D" were used for deposition of transparent and diffusing TiO_2 layers, respectively. Pastes, electrolyte "Iodolyte Z150", Pt catalyst "Platisol" and other components were purchased from Solaronix (Switzerland). The TiO_2

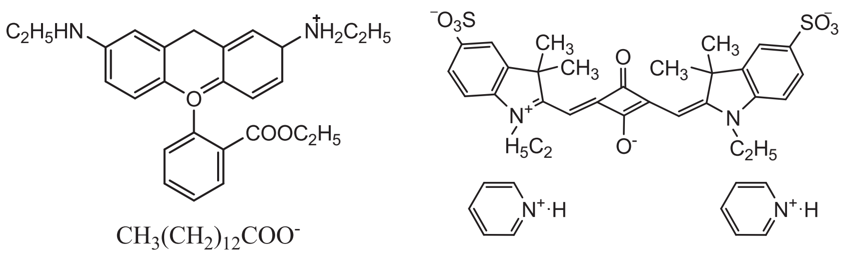
Fig. 2. Structure formulae of the donor (at the left) and acceptor of energy (at the right).